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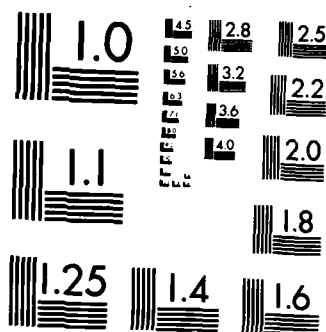UNCLASSIFIED CRDC-TR-84073 F/G 7/3 NL

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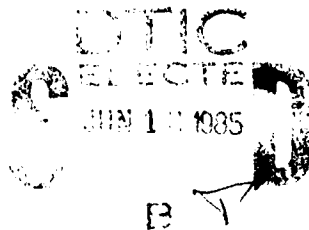NATIONAL BUREAU OF STANDARDS-1963-A

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SUCROSE HYDROLYSIS-TEMPERATURE DEPENDENCE OF THE ACTIVATION ENERGY

by   J. Richard Ward, Ph.D.

RESEARCH DIRECTORATE

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Sucrose hydrolysis is often cited as one of the classic examples of a chemical reaction with a temperature-dependent activation energy. Two different investigators, Moelwyn-Hughes (polarimetry) and Leininger and Kilpatrick (dilatometry), both claimed that the energy of activation decreased with increasing temperature. A less-cited paper by Heidt and Purvis claimed that the energy of activation was temperature independent. More recently, Kubler and co-workers at Furman University remeasured sucrose hydrolysis polarimetrically with correction made for the mutarotation lag and also concluded that the energy of activation did not vary with temperature.

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19.   ABSTRACT (continued)

Recent interest in the measurement and interpretation of heat capacities of activation
has led to more rigorous methods of detecting temperature varient activation parameters.
One such method by Blandamer, Robertson, and co-workers was applied to the sucrose
hydrolysis data of Moelwyn-Hughes and Leininger and Kilpatrick. It was found that the
data did not support the inclusion of a temperature-dependent activation energy.
Blandamer's method applied to Kubler's data also confirms the absence of any need to
include temperature-dependent activation parameters.

PREFACE

This work was performed under Project No. 1L161101A71A, Research in Defense Sciences. The work was started in October 1983 and completed in September 1984.

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SUCROSE HYDROLYSIS-TEMPERATURE DEPENDENCE
OF THE ACTIVATION ENERGY

INTRODUCTION

The hydrolysis of sucrose has a permanent place in the history physical chemistry since it was the first reaction studied as a func- on of time.[1] In addition, as Oon and Kubler note,[2] over 1,000 articles sucrose hydrolysis appeared by 1947. Despite this intense and ng-standing interest, questions persist relative to the mechanism of e reaction, particularly with regard to the temperature dependence of e activation energy. Moelwyn-Hughes[1] (polarimetry) and Leininger and lpatrick[3] (dilatometry) contend that the activation energy decreases th increasing temperature. Recently, Moelwyn-Hughes' results have en cited as the first example of a temperature-dependent activation ergy.[4] However, in 1939, Heidt and Purvis[5] claimed that the activation ergy was temperature independent based on a direct analysis of the oducts' reactions. More recently, Kubler and co-workers[6] remeasured e rate of sucrose hydrolysis polarimetrically, including a correction r the mutarotation of the products, and also monitored directly the oducts' rate of formation. These workers also contend that the tivation energy is not temperature dependent.

Since World War II, many examples of temperature-dependent tivation energies have been reported.[7,8] Concurrently, more rigorous thods have also been devised for detecting such temperature-dependent tivation parameters as opposed to the method both Moelwyn-Hughes and ininger and Kilpatrick used to determine the activation energies over rious temperature intervals.

In this article, the method proposed by Blandamer, Robertson, d co-workers[9] has been applied to Moelwyn-Hughes and Leininger and lpatrick's data to test their contention of a temperature-dependent tivation energy for sucrose hydrolysis.

BLANDAMER'S METHOD

Blandamer's expression for computing thermodynamic parameters om the temperature dependence of rate data is

$$k = \frac{k_o T}{T_o} \cdot \exp\left\{ \frac{\Delta H_o^{\ddagger}}{R} \left[\frac{1}{T_o} - \frac{1}{T} \right] + \frac{\Delta C_p^{\ddagger}}{R} \left[\ln\left(\frac{1}{T_o}\right) + \frac{T_o}{T} - 1 \right] \right\} \quad (1)$$

ere k = rate coefficient at temperature, T

T = temperature

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k_O = rate coefficient at temperature, T_O

$\Delta H_O^{\ddagger}$ = enthalpy of activation at T_O

$\Delta C_p^{\ddagger}$ = heat capacity of activation

Equation (1) is obtained by integrating the vant-Hoff isochore ~een temperatures T_O and T assuming $\Delta C_p^{\ddagger}$ independent of tempera- ~. For a given set of k, T data pairs, one pair of k and T are set ~o and T_O, and the remaining values of k, T are used in a regression ~quation (1) to find a value of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ at T_O. Another ~ of k, T are set as the new k_O, T_O and values of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ at new T_O are obtained. The process is repeated until each value of k, ~ the data set has been assigned k_O, T_O yielding values of $\Delta H^{\ddagger}$ $\Delta C_p^{\ddagger}$ for each temperature, T. Any data set produces:

(a) $\Delta C_p^{\ddagger}$ zero, $\Delta H^{\ddagger}$ constant with temperature,

(b) $\Delta C_p^{\ddagger}$ constant, $\Delta H^{\ddagger}$ linearly dependent with temperature,

(c) $\Delta C_p^{\ddagger}$ temperature dependent.

~tion (1) was derived with the assumption that $\Delta C_p^{\ddagger}$ is tem- ~ture independent, so for conditions (a) or (b) above, the values ~C_p are thermodynamically correct. However, Equation (1) gives ~correct sign for temperature dependent $\Delta C_p^{\ddagger}$ although the ~es so computed are not correct since the wrong equation is used ~ompute $\Delta C_p^{\ddagger}$. In order to find the values of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$, ~tion (1) is fit directly with a non-linear, least-squares program[10] ~pposed to the linear form of Equation (1) offered by Blandamer.[9] To ~her distinguish between conditions (a) and (b) above, the enthalpies ~ctivation so computed are fit versus temperature with a linear, ~t-squares version of the program to see if the slope differs from ~.

RESULTS AND DISCUSSION

The rate coefficients for sucrose hydrolysis are listed in ~e 1. These numbers were taken from Table 1 of Kubler's article ~erence 6). With the exception of Moelwyn-Hughes, all kinetic runs ~ done with 0.0584M sucrose in 0.57M HCl.

The following calculations were done on each k, T data set. ~es of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$, along with their respective standard ~vations of the mean, were computed at each temperature, T, with ~tion (1). The values of $\Delta H^{\ddagger}$, so generated, were fit with a ~ar, least-squares subroutine of the Los Alamos program[10] to

$$\Delta H^{\ddagger} = a + bT \qquad (2)$$

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Table 1. Summary of Rate Coefficients for
Inversion of 0.0584M Sucrose in 0.57M HCl[a]

T, °C	k[b]	T, °C	k[c]	T, °C	k[d]	T, °C	k[e]	T, °C	k[f]
0.0	0.291							0.0	0.303
10.0	1.65			9.92	1.609	9.60	1.609	10.0	1.69
15.0	3.66	15.54	3.58	14.68	3.444				
20.0	7.91	19.40	6.56	19.24	6.928	19.00	7.99		
25.0	16.5	23.09	11.6	24.97	16.07	23.20	13.79	23.4	13.3
30.0	33.5	26.26	20.5	29.96	32.69	24.77	17.3	30.05	34.9
35.0	65.6	31.08	34.3	35.00	67.79	29.82	36.5	30.05	34.9
40.0	129.0	35.98	64.8	40.02	129.3	34.97	71.9		
		41.00	124.0			39.80	137.0		

[a]units of k, s^{-1} x 10^5
[b]Leininger and Kilpatrick, Reference 3, dilatometry
[c]Moelwyn-Hughes, Reference 1, polarimetry uncorrected for mutarotation log in
5 percent sucrose solution at 0.2M HCl
[d]Kubler and co-workers, Reference 6, polarimetry corrected for mutarotation
log - duplicate runs
[e]Reference 7, chemical analysis of products
[f]Heidt and Purvis, Reference 5, chemical analysis of products
[g]Single determination of rate coefficient

idence intervals were computed with the "Student-t" statistic to
if values of $\Delta C_p^{\ddagger}$ or b differed significantly from zero.[11]   For
ercent confidence levels, values of t corresponding to α = 0.025
 n-p degrees of freedom were used, where n is the number of points
g fit, and p is the number of parameters being varied.[10] Finally,
entropy of activation was computed with

$$ k = \frac{\kappa t}{h} \exp \left(- \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \right) \tag{3} $$

e previously undefined parameters are κ = Boltzmann's constant, and
Planck's constant. Equation (3) presumes that $\Delta C_p^{\ddagger}$ is zero, and
aring values of k computed with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with experimental
es of k also tests whether $\Delta H^{\ddagger}$ is temperature independent.

The first calculations were done with Moelwyn-Hughes' data.
e 2 illustrates the values of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ obtained. In general,
$\Delta C_p^{\ddagger}$ values do not differ from zero. Results from fitting $\Delta H^{\ddagger}$
us T give a = 24.4 + 0.7 kcal/mole and b = -12.1 + 24.2 cal/mole -k,
esting that $\Delta H^{\ddagger}$ is independent of temperature. Table 3 lists the
lts of fitting K, T to Equation (3) to obtain ΔS. One sees that
computed values agree well with the experimental values except the
rimental values at the two lowest temperatures (15.45 and 19.40°C)
smaller than the computed values. Interestingly, if the mutarotation
had been taken into account, the experimental values at these tem-
tures would have been smaller.[6] This also coincides with Kubler's
rk[6] that a plot of ln k versus 1/T for Moelwyn-Hughes' data was
htly curved in the opposite direction to his own polarimetric
 uncorrected for mutarotation. Nonetheless, one concludes that
wyn-Hughes' data do not prove that $\Delta H^{\ddagger}$ varies with temperature.

The results of the next calculations which were made with
inger and Kilpatrick's rate data[3] are summarized in Table 4.
slope of a plot of $\Delta H^{\ddagger}$ versus T, -9.2 + 12.4 cal/mole -k also
ests that a temperature-independent $\Delta H^{\ddagger}$ is sufficient to represent
inger and Kilpatrick's data.[3]

Table 5 lists the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ computed with
inger and Kilpatrick's results, illustrating that the experimental
computed values of k agree within a few percent except for the value
.0°C which differs by 7 percent. Comparing Leininger and Kilpatrick's
lts with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ computed with Heidt and Purvis' results,
Kubler's polarimetric data illustrates that the fitted value of k
.0°C corresponds with Heidt and Purvis' measured value, and that the
es of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are identical to those computed with Kubler's
. Again, one concludes that Leininger and Kilpatrick's data do not
ort a temperature-dependent $\Delta H^{\ddagger}$.

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Table 2. Enthalpy of Activation Versus Temperature with
Moelwyn-Hughes' Data Obtained Polarimetrically[a]

T, °C	k_{obs}, s^{-1}	k_{fit}[a]	k_{fit}	k_{fit}	k_{fit}	k_{fit}	k_{fit}	k_{fit}
15.45	3.58	b	3.63	3.99	3.98	3.93	3.98	3.91
19.40	6.56	6.50	b	6.96	6.96	6.91	6.93	6.87
23.09	11.6	11.2	11.2	b	11.6	11.6	11.5	11.5
27.26	20.5	20.2	20.2	20.5	b	20.5	20.4	20.4
31.08	34.3	34.1	34.0	34.1	34.2	b	34.0	34.1
35.98	64.8	65.3	65.2	65.0	65.0	68.2	b	65.0
41.00	124.0	124.0	124.0	124.0	124.0	124.0	124.0	b
ΔH‡, cal/mole		24933.0	24455.0	23380.0	23613.0	23836.0	24155.0	24311.0
Std dev		201.0	199.0	153.0	179.0	162.0	727.0	169.0
ΔC$_p$‡, cal/mole-k		-35.5	-20.0	54.1[c]	49.7	28.7	62.0[c]	41.3
Std dev		16.8	19.6	18.1	27.3	34.0	21.9	27.2

[a]Units of rate coefficients are s^{-1} x 10^5.
[b]Rate coefficient fixed in Equation (1).
[c]Values of ΔC$_p$‡ significantly different from zero at the 95 percent confidence level.

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Table 3. Activation Parameters From Moelwyn-Hughes'
Results with $\Delta C_p^{\ddagger} = 0$

T, °C	k_{obs}, s^{-1} x 10^5	k_{fit}, s^{-1} x 10^5
15.45	3.58	3.75
19.40	6.56	6.70
23.09	11.6	11.4
27.26	20.5	20.3
31.08	34.3	34.1
35.98	64.8	65.2
41.00	124.0	124.0

$\Delta H^{\ddagger} = 24.07 \pm 0.09$ kcal/mole

$\Delta S^{\ddagger} = 4.05 \pm 0.3$ cal/mole-k

Table 4. Enthalpy of Activities Versus Temperature with Leininger and Kilpatrick's Data

T, °C	k_{obs}, s⁻¹×10⁵	k_{fit}[a]	k_{fit}	k_{fit}	k_{fit}	k_{fit}	k_{fit}	k_{fit}	k_{fit}
0.0	0.291	b	0.313	0.323	0.352	0.391	0.375	0.406	0.376
10.0	1.65	1.59	b	1.67	1.74	1.84	1.82	1.86	1.80
15.0	3.66	3.56	3.63	b	3.75	3.88	3.88	3.89	3.83
20.0	7.91	7.70	7.77	7.81	b	8.07	8.11	8.04	8.00
25.0	16.5	16.2	16.2	16.3	16.3	b	16.6	16.4	16.4
30.0	33.5	33.1	33.1	33.1	33.1	33.2	b	33.0	33.2
35.0	65.6	66.2	66.1	66.0	65.9	65.9	66.3	b	65.9
40.0	129.0	129.0	129.0	129.0	129.0	129.0	129.0	129.0	b
$\Delta H^{\ddagger}$, cal/mole		25686.0	24990.0	24826.0	24535.0	24400.0	24627.0	25130.0	25270.0
std dev		152.0	147.0	151.0	148.0	168.0	190.0	81.0	167.0
$\Delta C_p^{\ddagger}$, cal/mole-k		-19.6	1.1	10.1	32.9	57.3	35.5	75.5[c]	49.7
std dev		8.2	10.0	12.9	16.0	23.5	39.0	24.0	27.0

[a] Fitted values of k, s⁻¹×10⁵

[b] Rate coefficient fixed

[c] Significant at 95 percent confidence level

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Table 5. Activation Parameters for Inversion of 0.0584M Sucrose in 0.57M HCl

T, °C	k, s^{-1} x 10^5[a]	k_{fit}, s^{-1} x 10^5	T, °C	k, s^{-1} x 10^5[b]	k_{fit}, s^{-1} x 10^5	T, °C	k, s^{-1} x 10^5[c]	k_{fit}, s^{-1} x 10^5
0.0	0.291	0.315	0.0	0.303	0.309	9.92	1.609	1.670
10.0	1.65	1.66	10.0	1.69	1.66	14.68	3.444	3.528
15.0	3.66	3.65	23.4	13.3	13.3	19.24	6.928	7.063
20.0	7.91	7.81	30.05	34.9	34.9	24.97	16.07	16.40
25.0	16.5	16.3				29.96	32.39	33.29
30.5	33.5	33.2				35.00	67.79	66.52
35.0	65.6	66.1				40.02	12.93	12.97
40.0	129.0	129.0						
ΔH‡, cal/mole	25.0			25.3			24.9	
std dev[d]	0.1			0.1			0.3	
ΔS‡, cal/mole-k	7.9			9.1			7.6	
std dev[d]	0.3			0.1			0.9	

[a] Leininger and Kilpatrick, Reference 3

[b] Heidt and Purvis, Reference 5

[c] Kubler, Reference 7

[d] Standard deviation of the mean as computed by least-squares program

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For completeness, similar computations were done to Kubler's data and to Heidt and Purvis' results. In both instances, the fit of $\Delta H^{\ddagger}$ versus T shows that the slope, b, is zero, and $\Delta H^{\ddagger}$ is temperature independent, in accordance with each investigator's contention.

4.   CONCLUSION

Blandamer and Robertson's equation for determining heat capacities of activation was applied to Moelwyn-Hughes' and to Leininger and Kilpatrick's data on sucrose hydrolysis. There was no evidence for a finite heat capacity of activation in either case.

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